

PASSIVATION COMPOSITION AND PROCESS FOR ZINCIFEROUS AND ALUMINIFEROUS SURFACES

BACKGROUND OF THE INVENTION

This application claims the benefit of U.S. Provisional Patent
5 Application Serial No. 60/426,477, filed on November 15, 2002.

1. Field of the Invention

In at least one aspect, the present invention relates to compositions
and processes for passivating, i.e., forming a corrosion protective surface layer, on
metal surfaces that consist predominantly of aluminum and/or zinc. A wide variety
10 of such surfaces are in normal use, including many kinds of galvanized and/or
aluminized steel, and the invention is applicable to such surfaces which differ from
the underlying metal, as well as to solid alloys of aluminum and/or zinc.

2. Background Art

Zinc (zinciferous) and zinc alloy (such as aluminiferous) coatings are
15 frequently used to protect steel from corrosion. Two common types of metal-coated
steel typically used are galvanized steel (zinc) and Galvalume® (55% Al, 43.5% Zn,
1.5% Si). Both galvanized steel and Galvalume® have long service lifetimes as a
result of galvanic and/or sacrificial corrosion protection afforded by the coatings.
While the underlying steel is protected, the zinc coating is sometimes susceptible to
20 corrosion that can result in surface staining and white corrosion.

Traditionally, most zinciferous and/or aluminiferous surfaces have
been passivated by chemical treatment with aqueous liquid compositions containing
at least some hexavalent chromium. However, the adverse environmental effects of
hexavalent chromium that have come to public attention in recent years have

resulted in development of alternative, chromium-free compositions for this purpose. As such, what is needed is a composition and process for passivating metal surfaces that consist predominantly of aluminum and/or zinc that overcomes at least one constraint in the prior art.

5

SUMMARY OF THE INVENTION

In at least one aspect of the invention, an entirely or substantially chromium-free composition and process for passivating is provided that provides adequate corrosion resistance in comparison with previously used chromate containing passivating agents.

10

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

Reference will now be made in detail to presently preferred compositions or embodiments and methods of the invention, which constitute the best modes of practicing the invention presently known to the inventors.

15

It has been found that one or more of the objects stated above for the invention can be achieved by the use of a passivating aqueous liquid composition that comprises, preferably consists essentially of, or more preferably consists of, water and:

(A) dissolved phosphate anions; and

20

(B) dissolved fluorometallate anions selected from the group consisting of TiF_6^{-2} , ZrF_6^{-2} , HfF_6^{-2} , SiF_6^{-2} , AlF_6^{-3} , GeF_6^{-2} , SnF_6^{-2} , BF_4^- , and mixtures thereof.

The above composition may optionally further comprises one or more of the following:

- (C) an amino-phenolic polymer component;
- (D) a pH adjusting component; and
- 5 (E) a wetting agent.

Various embodiments of the invention include working compositions for direct use in treating metals, make-up concentrates from which such working compositions can be prepared by dilution with water, replenisher concentrates suitable for maintaining optimum performance of working compositions according to the invention, processes for treating metals with a composition according to the invention, and extended processes including additional steps that are conventional per se, such as cleaning, rinsing, and subsequent painting or some similar overcoating process that puts into place an organic binder-containing protective coating over the metal surface treated according to a narrower embodiment of the invention. Articles of manufacture including surfaces treated according to a process of the invention are also within the scope of the invention.

Except in the operating examples, or where otherwise expressly indicated, all numerical quantities in this description indicating amounts of material or conditions of reaction and/or use are to be understood as modified by the word "about" in describing the broadest scope of the invention. Practice within the numerical limits stated is generally preferred. Also, unless expressly stated to the contrary: percent, "parts of", and ratio values are by weight; the term "polymer" includes "oligomer", "copolymer", "terpolymer", and the like; the description of a group or class of materials as suitable or preferred for a given purpose in connection with the invention implies that mixtures of any two or more of the members of the group or class are equally suitable or preferred; description of

constituents in chemical terms refers to the constituents at the time of addition to any combination specified in the description, and does not necessarily preclude chemical interactions among the constituents of a mixture once mixed; specification of materials in ionic form implies the presence of sufficient counter-ions to produce electrical neutrality for the composition as a whole (any counter-ions thus implicitly specified should preferably be selected from among other constituents explicitly specified in ionic form, to the extent possible; otherwise such counter-ions may be freely selected, except for avoiding counter-ions that act adversely to the objects of the invention); the first definition of an acronym or other abbreviation applies to all subsequent uses herein of the same abbreviation and applies mutatis mutandis to normal grammatical variations of the initially defined abbreviation; the term "paint" includes all like materials that may be designated by more specialized terms such as lacquer, enamel, varnish, shellac, topcoat, and the like; and the term "mole" and its variations may be applied to elemental, ionic, and any other chemical species defined by number and type of atoms present, as well as to compounds with well defined molecules.

For a variety of reasons, it is sometimes preferred that compositions according to the invention as defined above should be substantially free from many ingredients used in compositions for similar purposes in the prior art. Specifically, when maximum storage stability of a concentrate, avoidance of possibly troublesome anions, and/or minimization of pollution potential is desired, it is preferred, with increasing preference in the order given, independently for each preferably minimized component listed below, that these compositions contain no more than 25, 15, 9, 5, 3, 1.0, 0.35, 0.10, 0.08, 0.04, 0.02, 0.01, 0.001, or 0.0002 percent of each of the following constituents: nitrite; halates and perhalates (i.e., perchlorate, chlorate, iodate, etc.); hydroxylamine and salts and complexes of hydroxylamine; chloride; bromide; iodide; organic compounds containing nitro groups; hexavalent chromium; ferricyanide; ferrocyanide; and pyrazole compounds. Components such as these may not be harmful in some instances, but they have not been found to be needed or advantageous in compositions according to this

invention, and their minimization is therefore normally preferred at least for reasons of economy.

5 The dissolved phosphate ions that constitute necessary component (A) may be obtained from a variety of sources as known in the art. Normally much of the phosphate content will be supplied by phosphoric acid added to the composition, and the stoichiometric equivalent as phosphate ions of all undissociated phosphoric acid and all its anionic ionization products in solution, along with the stoichiometric equivalent as phosphate ions of any dihydrogen phosphate, monohydrogen phosphate, or completely neutralized phosphate ions added to the composition in salt form, are to be understood as forming part of phosphate ions component (A), 10 irrespective of the actual degree of ionization and/or reaction to produce some other chemical species that exists in the composition. If any metaphosphoric acid, other condensed phosphoric acids, or salts of any of these acids are present in the compositions, their stoichiometric equivalent as phosphate is also considered part of component (A). Generally, however, it is preferred, at least partly for reasons of 15 economy, to utilize orthophosphoric acid and its salts as the initial source for component (A).

20 In a working passivating aqueous liquid composition according to the invention, the concentration of phosphate ions and/or their stoichiometric equivalents as noted above preferably is at least, with increasing preference in the order given, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 9.0, 10.0, 12.0, 13.0, 14.0, 15.0, 16.0 or 17.0 grams per liter (hereinafter usually abbreviated as "g/L") of total composition and independently preferably is not more than, with increasing preference in the order given, 400, 200, 100, 90, 80, 75, 70, 60, 50, 45, 40 or 34 g/L.

25 The dissolved fluorometallate anions that constitute necessary component (B) preferably are selected from the group consisting of TiF_6^{-2} , ZrF_6^{-2} , HfF_6^{-2} , SiF_6^{-2} , AlF_6^{-3} , GeF_6^{-2} , SnF_6^{-2} , BF_4^- , and mixtures thereof, with the first two being more preferred and fluorotitanate being the most preferred. Such anions may

be introduced into a treatment composition according to the invention as acids or salts, with the acids usually preferred for economy and because a net acidity of the compositions is preferable as considered further below, and the entire stoichiometric equivalent as any of the above recited fluorometallate ions in any source material as dissolved in a composition according to the invention or a precursor composition for it is to be considered as part of the fluorometallate component, irrespective of the actual degree of ionization that may occur. Independently of their chemical nature, the total concentration of the fluorometallate anions dissolved in a working treatment composition according to the invention preferably is at least, with increasing preference in the order given, 0.5, 1.0, 2.0, 2.5, 3.0, 4.0, 5.0, 6.0, 7.5, 8.5, 10.0, 11.0, 12.0 or 13.0 g/L and independently, primarily for reasons of economy, preferably is not more than, with increasing preference in the order given, 400, 200, 100, 90, 80, 75, 65, 50, 45, 38, 37.5, 35.0, 32.5 30.0, 28.0, 27.0 or 26.0 g/L.

Furthermore, independently of their actual concentrations, the concentrations of fluorometallate anions (B) and phosphate ions (A) preferably are such that the ratio between them, in working compositions and concentrated solutions used to prepare working concentrations, is at least, with increasing preference in the order given, 0.10:1.0, 0.15:1.0, 0.25:1.0, 0.35:1.0, 0.45:1.0, 0.50:1.0, 0.55:1.0, 0.60:1.0, 0.65:1.0, or 0.75:1.0 and independently preferably is not more than, with increasing preference in the order given, 5:1.0, 4:1.0, 3.5:1.0, 3.2:1.0, 2.0:1.0, 1.5:1.0, 1.0:1.0, or 0.9:1.0.

The composition of the present invention also optionally includes an amino-phenolic polymer component (C). Suitable examples of such polymers include Mannich adducts of secondary amines containing a carbon chain with at least one hydroxy group, formaldehyde, and a polyphenolic resin. In some embodiments, polymer composition (C) is selected from the group consisting of water soluble and water dispersible polymers and copolymers of one or more x -(N-R¹ -N-R² -aminomethyl)-4-hydroxy-styrenes, where $x=2, 4, 5$, or 6 , R¹ represents an alkyl

group containing from 1 to 4 carbon atoms, preferably a methyl group, and R^2 represents a substituent group conforming to the general formula $H(CHOH)_nCH_2-$, where n is an integer from 1 to 7, preferably from 3 to 5. Certain preferred polymers are Mannich adducts of polyvinyl phenol that are described in more detail in U.S. Patent Nos. 4,376,000; 4,433,015; 4,457,790; 4,517,028; 4,963,596; 4,970,264; 5,039,770; 5,068,299; 5,116,912; 5,266,410; 5,298,289; and 5,891,952, the entire disclosure of each patent, except to the extent contrary to any explicit statement herein, is hereby incorporated herein by reference. In certain embodiments, the polymer component (C) is the Mannich adduct of polyhydroxystyrene with N-methylglucamine. Polymer (C), in some embodiments, can also be added as a solution of the polymer component with an acid, such as fluorotitanic acid, phosphoric acid, and fluoro-zirconic acid. In these embodiments, the concentrations of polymer (C) and the acid in the polymer (C)/acid solution preferably are such that the ratio between them is at least, with increasing preference in the order given, 1.0:1.0, 2.0:1.0, 3.0:1.0, 4.0:1.0, 5.0:1.0, 5.0:1.0 or 6.5:1.0, and independently preferably is not more than, with increasing preference in the order given, 50:1.0, 40:1.0, 30:1.0, 25:1.0, 15:1.0, 10:1.0, 9.0:1.0, 8.0:1.0 or 7.5:1.0. When polymer (C) is used, independently of their chemical nature, the total concentration of the polymer (C) dissolved in a working treatment composition according to the invention preferably is at least, with increasing preference in the order given, 0.1, 0.25, 0.50, 0.75, 1.0, 1.25, 1.50 or 1.70 g/L of total composition and independently preferably not more than, with increasing preference in the order given, 150, 100, 75, 50, 25, 15 or 13 g/L. The optimal amount of polymer (C) depends in large part on the desired end property of the coating. If relatively significant corrosion protection is considered more important than ease of coating removability, then a relatively higher amount of polymer (C) can be used, however, if ease of coating removability is considered more important than corrosion protection, then a relatively smaller amount of polymer (C) can be used.

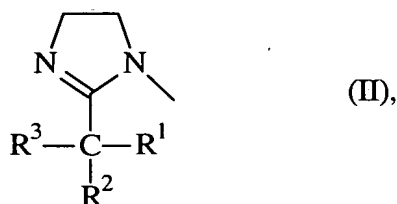
Furthermore, when polymer (C) is used, independently of their actual concentrations, the concentrations of polymer (C) and phosphate anions (A)

preferably are such that the ratio between them, in working compositions and concentrated solutions used to prepare working concentrations, is at least, with increasing preference in the order given, 0.005:1.0, 0.01:1.0, 0.015:1.0, 0.02:1.0, 0.025:1.0, 0.03:1.0, 0.035:1.0, 0.04:1.0, 0.045:1.0 or 0.05:1.0, and independently
5 preferably is not more than, with increasing preference in the order given, 1.2:1.0, 1.0:1.0, 0.90:1.0, 0.75:1.0, 0.60:1.0, 0.50:1.0, 0.45:1.0, 0.35:1.0, 0.25:1.0, 0.20:1.0, 0.10:1.0 or 0.07:1.0.

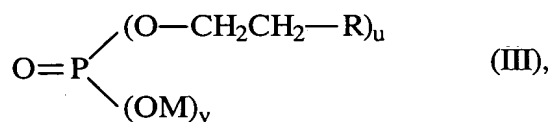
The *pH* of the treatment bath should be from 1.0 to 4.0, more preferably 1.2 to 2.5, and most preferably from 1.5 to 2.0. A *pH* below 1.0 may
10 result in an overly strong etch and scanty coating formation. At a *pH* in excess of 4.0, the solution may have a pronounced tendency to form precipitates, which can result in a shortened bath life. The *pH* can be adjusted using a pH adjusting component (D) such as an acid such as phosphoric acid, or nitric acid, or a base
15 such as sodium hydroxide, potassium hydroxide, sodium carbonate, or ammonium hydroxide, with ammonium hydroxide being the most preferred. When the pH adjusting component (D) is used, independently of their chemical nature, the total concentration of pH adjusting component (D) dissolved in a working treatment
composition according to the invention preferably is at least, with increasing preference in the order given, 1.0, 5, 10, 15, 20, 25, 30, or 32.5 g/L of total
20 composition, and independently preferably not more than, with increasing preference in the order given, 100, 90, 80, 75, 70, 60, 50, or 45 g/L.

The composition of the present invention also optionally includes a wetting agent (E). The wetting agent (E) is particularly useful for wetting surfaces that are known to be somewhat difficult to wet, such as Galvalume®. Wetting
25 agents that improve coating wetting without increasing water sensitivity of the composition and that are soluble and stable in strong acidic solutions are preferred. Examples of suitable wetting agents include, but are not limited to, phosphate esters. Preferred phosphate esters include, but are not limited to, substituted phosphate esters, and more preferably substituted carboxylated phosphate esters. A

particularly preferred wetting agent (E) is PHOSPHOTERIC™ TC-6. PHOSPHOTERIC™ TC-6 is reported by its supplier, Uniqema of New Castle, Delaware, to have an "R" moiety according to chemical formula (II):



where at least one of R^1 and R^3 is carboxyethyl or salt thereof and the other is carboxyethyl, salt thereof, or hydrogen, and R^2 is coconut oil alkyl, in chemical formula (III):



where u is 1 or 2, $y = (4-u)$, and M is hydrogen or sodium cation, except that at least one M must be sodium cation.

When this component (E) is used, independently of their chemical nature, the total concentration of wetting agent (E) dissolved in a working composition according to the invention, preferably is at least, with increasing preference in the order given, 0.10, 0.20, 0.25, 0.30, 0.40, 0.50, 0.55, 0.60 or 0.65 g/L of total composition and independently preferably not more than, with increasing preference in the order given, 5.0, 4.0, 3.0, 2.5, 2.0, 1.5, 1.0, 0.90, 0.80 or 0.75 g/L.

Furthermore, when wetting agent (E) is used, independently of their actual concentrations, the concentrations of wetting agent (E) and phosphate anions (A) preferably are such that the ratio between them, in working compositions and

concentrated solutions used to prepare working compositions, is at least, with increasing preference in the order given, 0.010:1.0, 0.015:1.0, 0.020:1.0 or 0.025:1.0 and independently preferably is not more than, with increasing preference in the order given, 0.20:1.0, 0.15:1.0, 0.10:1.0, 0.090:1.0, 0.075:1.0, 0.060:1.0, 5 0.050:1.0, 0.045:1.0, 0.040:1.0 or 0.035:1.0.

The most preferred components are as follows:

Component	Trade Name	Supplier	CAS No.
A	Phosphoric Acid (75% by weight)	Lidchem, Hazlet, NJ	7664-38-2
B	Hexafluorotitanic Acid (50% by weight)	GE Honeywell, Morristown, NJ	17439-11-1
10 C	TD-1355-DE (about 10% by weight non-volatiles) ¹	Henkel Corp.	
D	Ammonium Hydroxide (29% by weight)	Sigma-Aldrich, St. Louis, MO	1336-21-6
E	Phosphoteric™ TC-6 (35% by weight)	Uniqema, Chicago, IL	

The composition of the present invention can be prepared by combining the components in any order.

¹ TD-1355-DE is an aqueous solution containing about 1.2 wt. % hexafluorotitanic acid and about 8.6 wt. % of a Mannich adduct of polyhydroxystyrene, N-methylglucamine, and formaldehyde prepared in accordance with U.S. Patent No. 5,891,952.

Some preferred concentrated compositions, in accordance with the present invention, comprise:

5

Component	Preferred Wt. % Range	More Preferred Wt. % Range	Most Preferred Wt. % Range
A	25 - 65	35 - 55	46 - 47
B	35 - 75	45 - 65	53 - 54

Other preferred concentrated compositions, in accordance with the present invention, comprise:

10

Component	Preferred Wt. % Range	More Preferred Wt. % Range	Most Preferred Wt. % Range
A	8.0 - 65.0	12.5 - 40.0	15.0 - 34.0
B	10.0 - 75.0	10.0 - 35.0	13.0 - 30.0
C	0 - 80.0	5.0 - 70.0	22 - 67
D	0 - 7.5	2.0 - 5.0	3.5 - 4.5
E	0 - 3.5	0.5 - 2.5	1.0 - 2.0

15

For use as working compositions, the concentrated composition is typically diluted, with water, to about 2-50 wt. %, more preferably 3.5-30 wt. %, and most preferably about 5-20 wt. %.

Some particularly preferred working compositions, in accordance with the present invention, comprise:

5

Component	Preferred Wt. % Range	More Preferred Wt. % Range	Most Preferred Wt. % Range
A	1.0 - 15.0	2.0 - 10.0	3.0 - 5.0
B	1.0 - 20.0	2.0 - 15.0	3.0 - 4.0
C	0 - 40.0	1.0 - 25.0	2.0 - 17.5
D	0 - 2.5	0.1 - 1.0	0.3 - 0.5
E	0 - 1.2	0.01 - 0.80	0.1 - 0.6
DI Water	45 - 98	60 - 92	72 - 91

10

It should be appreciated that the weight percents in the three preceding tables are on a wet basis and that the components referred to in those tables have percent solids similar to the percent solids of the components listed in the table preceding the above three tables.

15

20

A process according to the invention in its simplest form consists of bringing a metal surface to be passivated into physical contact with a working composition according to the invention as described above for a period of time, then discontinuing such contact and drying the surface previously contacted. Suitable metal surfaces include galvanized and/or aluminized steel, and solid alloys of aluminum and/or zinc. Physical contact and subsequent separation can be accomplished by any of the methods well known in the metal treatment art, such as immersion for a certain time, then discontinuing immersion and removing adherent liquid by drainage under the influence of natural gravity or with a squeegee or similar device; spraying to establish the contact, then discontinuing the spraying and removing excess liquid as when contact is by immersion; roll coating of the amount of liquid followed by drying into place, and the like.

25

Preferably the temperature of the working passivating aqueous liquid composition during a passivation process according to the invention is at least, with increasing preference in the order given, 15°C, 20°C, 25°C, 30°C, 34°C or 37°C.

and independently preferably, primarily for reasons of economy, is not more than 66°C, 60°C, 55°C, or 50°C. The quality of the passivation layer formed is not known to be substantially affected by the temperature during passivating if the temperature is within any of these preferred limits; the primary reason for the preference for a minimum temperature during passivating that is greater than the normal ambient temperature is that with such a passivating temperature and squeegeeing off of any adherent liquid promptly after discontinuing contact of the surface to be passivated with a working passivating aqueous liquid composition according to the invention, the surface will dry spontaneously in ambient air within a few seconds to form a passivated surface according to the invention. This method of operation is particularly well adapted to most existing coil processing plants.

The time during which physical contact is maintained between the metal surface to be passivated and a working passivating aqueous liquid composition according to the invention preferably, for reasons of economy of operation, is as short as possible, consistent with formation of a passivating layer as effective as desired. More specifically, the time of contact preferably is not more than, with increasing preference in the order given, 200, 150, 100, 75, 50, 40, 30, 25, 20, 15, 13, 11, 10, 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0, 1.5, 1.0, 0.5 or 0.1 seconds. Spraying a heated working passivating aqueous liquid composition onto the surface to be passivated followed by removing excess liquid with a squeegee has been found effective in forming a passivated surface according to this invention within a few seconds at most.

Normally the surface to be passivated preferably is not rinsed with water or other diluent between contact with a working passivating aqueous liquid composition according to the invention and drying. Drying can be accomplished by simple exposure to ambient air for a sufficient time, and indeed is preferably accomplished in this way if the passivated surface has been formed at a sufficiently high temperature that drying occurs within a few seconds of separation from contact with the working passivating aqueous liquid composition according to the invention

as described above. Alternatively, one may hasten the drying by exposure of the wet surface after passivation to a higher temperature than the normal ambient temperature, in an oven or by any of the other means such as infrared radiant heating, microwave drying, and the like well known per se in the art.

5 Preferably, the coating is thick enough that aqueous liquid composition according to the invention corresponds to at least, with increasing preference in the order given, 5, 10, 15, 20, 21.5, 30, 38, 43, 50, 60, or 64.6 milligrams per square meter of the metal surface passivated (hereinafter usually abbreviated as "mg/m²"), measured as total weight of the coating, and
10 independently, preferably is not more than, with increasing preference in the order given, 600, 575, 540, 450, 300, 200, 172, 150, 129, 115, 100, or 90 mg/m² measured as total weight of the coating. The amount of total coating weight added-on may conveniently be measured with commercially available instruments, or by other means known to those skilled in the art.

15 Preferably, the coating is thick enough that aqueous liquid composition according to the invention corresponds to at least, with increasing preference in the order given, 0.24, 0.5, 1.0, 2.0, 4.0, 6.0, or 8.0 milligrams per square meter of the metal surface passivated (hereinafter usually abbreviated as "mg/m²"), measured as titanium atoms, and independently preferably corresponds
20 to not more than 133, 125, 100, 75, 50, 40, 24, or 17 mg/m² measured as Titanium atoms. The amount of titanium added-on may conveniently be measured with a commercially available instrument, a PORTASPEC™ Model 2501 X-ray spectrograph from Cianflone Scientific, or by other means known to those skilled in the art.

25 After forming the initial passivating layer as described above, it is sometimes preferred to further improve the corrosion and/or staining resistance of the passivated surface face by overcoating it with a protective layer containing at least an organic binder. It is presently contemplated that any of a wide variety of

clear and pigmented paints and like materials, as generally known per se in the art can be used for this purpose. Such an overcoating preferably has a thickness after drying that is at least, with increasing preference in the order given, 0.2, 0.4, 0.6, 0.8, or 1.0 micrometers (hereinafter usually abbreviated as " μm ") and independently preferably, primarily for reasons of economy, is not more than 10, 7, 5, 3, 2.5, 2.0, 1.5, or 1.3 μm . When the passivated surface is to be used in an application where a metallic appearance is desired, as in roofing for example, this relatively thin clear overcoating can serve adequately as the final coating layer in many instances. For more severe service, additional thicker coatings of paint and like materials adapted to a specific purpose as known per se in the art may be applied directly over this initial thin acrylic overcoating, or directly over the passivated metal surface itself.

In certain embodiments, the passivated surface may remain uncovered, i.e., not painted.

In certain other embodiments, the passivating coating can act as a temporary coating. In this embodiment, the passivating coating is intended to provide temporary corrosion protection for preventing corrosion and staining during the time period after galvanizing and prior to final finishing, i.e., during storage and shipping. The passivating coating could then be removed and the substrate coated with a more permanent corrosion resistant coating, as is known in the art. For instance, the more permanent corrosion resistant coatings can be provided by a suitable conversion coating process. Suitable conversion coating composition and processes are disclosed in U.S. Patent Nos. 4,961,794; 4,838,957; 5,073,196; 4,149,909; 5,356,490; 5,281,282; and 5,769,967, which are hereby incorporated by reference. In this embodiment, if the passivating coating is to be removed, it is presently contemplated that this can be readily done by exposing the passivating coating to a suitable alkaline cleaner solution.

Before passivating according to this invention is to be used for any metal substrate, the substrate to be passivated may, but is not necessarily, thoroughly cleaned by any of various methods well known to those skilled in the art to be suitable for the particular substrate to be coated.

5 Where galvanized metal surfaces are mentioned in connection with the present invention, they are understood to be material surfaces of electrolytically galvanized or hot-dip-galvanized or even alloy-galvanized steel, preferably electrolytically galvanized or hot-dip-galvanized steel strip. By steel is meant
10 unalloyed to low-alloyed steel of the type used, for example, in the form of sheets for automotive bodywork. The use of galvanized steel, particularly electrolytically galvanized steel in strip form, has grown considerably in significance in recent years. The expression "galvanized steel" in the context of the present invention is understood to encompass electrolytically galvanized steel and also hot-dip-galvanized steel and also applies generally to alloy-galvanized steel, zinc/nickel
15 alloys, zinc/iron alloys (Galvanealed) and zinc/aluminum alloys (GALFAN®, from Eastern Alloys, Inc., of Maybrook, New York, GALVALUME™, from BIEC International, Inc. of Vancouver, Washington) playing a particularly crucial role as zinc alloys.

20 The practice of this invention may be further appreciated by consideration of the following, non-limiting examples, and the benefits of the invention may be appreciated by the examples set forth below.

Examples

Example 1

Working compositions 1 and 2 were prepared as set forth below in Table 1.

TABLE 1
Passivate Compositions

	Composition 1 (pH ~ 1.7) wt. (g)	Composition 2 (pH ~ 1.7) wt. (g)
Ingredient		
DI Water	92.5	77.5
75% H ₃ PO ₄	3.5	4.0
50% H ₂ TiF ₆	4.0	3.5
TD-1355-DE (10% solids)	-	15.0

Test panels of HDG (hot dipped galvanized) steel and Galvalume® steel were prepared in the following manner.

The HDG steel panels were cleaned with a 3 wt. % solution of Parco® Cleaner 1200, available from Henkel Corporation, at a temperature of about 140°F for about 20 seconds. The panels were then hot water rinsed at a temperature of about 120°F for about 10 seconds. The panels were then squeegeed dry. Compositions 1 and 2 were then diluted to about 66 wt. % and were then applied to the panels using a No. 3 draw bar. The panels were then dried in an IR oven. The total coating weight on the panels were about 4-8 mg/ft².

Galvalume® steel panels were cleaned and treated in the same manner except they were only cleaned for about 7 seconds.

The panels, along with bare test panels, were submitted for 168 hours of NSS (Neutral Salt Spray) testing in accordance with ASTM B117-90 and 240

hours of Cleveland Condensing Humidity testing in accordance with ASTM D4585-87. The results are shown below in Tables 2 and 3.

TABLE 2
168-Hour Neutral Salt Spray Test Results.
Compositions 1 and 2
vs. bare samples

168 Hrs of Neutral Salt Spray		
Composition	Substrate	% White Rust
1	Galvalume®	50 %
1	HDG	100 % after 48 hrs
2	Galvalume®	33 %
2	HDG	33 % after 48 hrs
Bare	Galvalume®	100 % * after 24 hrs
Bare	HDG	100 % after 5 hrs

*Represents Black Rust

TABLE 3
240-Hour Cleveland Condensing Humidity Test Results
Compositions 1 and 2
vs. bare samples

240 Hrs of Cleveland Condensing		
Composition	Substrate	% White Rust
1	Galvalume®	< 1 %
1	HDG	50 % after 72 hrs
2	Galvalume®	3 %
2	HDG	13 %
Bare	Galvalume®	100 % * after 48 hrs
Bare	HDG	100 % after 5 hrs

* Represents Black Rust

Example 2

Working compositions 3 and 4 were prepared as set forth below in Table 4.

TABLE 4

Passivate Compositions

	Composition 3 (pH ~ 1.7) wt. (g)	Composition 4 (pH ~ 1.7) wt. (g)
Ingredient		
DI Water	945.0	90.5
75% H ₃ PO ₄	25.0	4.0
50% H ₂ TiF ₆	30.0	3.5
TD-1355-DE (10% solids)	-	2.0

HDG and Galvalume® steel test panels were prepared and subjected to NSS testing for 336 hours in the manner set forth above in Example 1. The results are shown below in Table 5.

TABLE 5

NEUTRAL SALT SPRAY TESTING RESULTS ON GALVALUME AND HDG:

					% WHITE RUST							
					Day1	Day2	Day3	Day4	Day5	Day6	Day7	Day14
Panel#	Composition	Substrate	Application	Appearance	24	48	72	96	120	144	168	336
13	3	Galvalume®	#3db	Splotchy	1	1	3	3	10	33	33	100
14			4-6 mg/ft ²		1	1	3	10	33	33	33	100
15			Coating wt.		0	0	1	3	10	33	33	50

						% WHITE RUST							
						Day1	Day2	Day3	Day4	Day5	Day6	Day7	Day14
5	Panel#	Composition	Substrate	Application	Appearance	24	48	72	96	120	144	168	336
	16	3	Galvalume®	coater	Perfect	3	100	100	100	100	100	100	100
	17			2-4 mg/ft ²		3	100	100	100	100	100	100	100
10	18			Coating wt.		3	100	100	100	100	100	100	100
	28	4	Galvalume®	#3db	Perfect	0	0	0	0	0	0	0.1	1
	29			4-8 mg/ft ²		0	0	0	0	0.1	0.1	0.1	1
15	30			Coating wt.		0	0	0	0	0	0	0.1	3
	110	1	Galvalume®	#3db	Perfect	0	0	0	1	3	5	10	100
	111			4-8 mg/ft ²		0	0	1	1	5	5	10	100
20	112			Coating wt.	Dark	0	1	1	5	5	5	3	100
	113	2	Galvalume®	#3db	Splotchy	1	1	1	1	1	1	1	100
	114			4-8 mg/ft ²		1	1	1	1	1	1	1	50
25	115			Coating wt.		1	1	1	1	3	3	3	100
	40	1	HDG	#3db	Uneven	16	100	100	100	100	100	100	100
	41	66%sol.		2-4 mg/ft ²	edges	16	100	100	100	100	100	100	100
30	42			Coating wt.		10	33	33	100	100	100	100	100
	43	1	HDG	#3db	Perfect	1	16	50	100	100	100	100	100
	44	66%sol.		2-4 mg/ft ²		1	33	50	100	100	100	100	100
35	45			Coating wt.		1	10	33	100	100	100	100	100
	67	3	HDG	coater	Splotchy	16	100	100	100	100	100	100	
	68			2-4 mg/ft ²		33	100	100	100	100	100	100	
40	69			Coating wt.		33	100	100	100	100	100	100	
	82	4	HDG	#3db	Near	3	16	50	50	50	100	100	
	83			4-8 mg/ft ²	Perfect	1	50	100	100	100	100	100	
45	84			Coating wt.		3	50	100	100	100	100	100	

Example 3

HDG and Galvalume® steel test panels were cleaned with a 4 wt. % solution of Ridoline® 321 at a temperature of about 140°F for about 30 seconds. The panels were then hot water rinsed at a temperature of about 120°F for about 10 seconds. The panels were then squeegeed dry. Composition 1 was applied to the panels using various drawbars. The test panels were then subjected to (i) Stack testing, (ii) Butler Water Immersion testing, and (iii) NSS testing for 72 hours in the

manner set forth above in Example 1. The results are shown below in Tables 6, 7, and 8.

TABLE 6
Stack Test Results

(% Black Rust (BR) White Rust (WR))

Substrate/ Coating method	Total Coat. Wt. (mg/ft ²)	168 Hrs		336 Hrs		672 Hrs	
		BR	WR	BR	WR	BR	WR
HDG (#9 drawbar)	8-12	0	0	1	10	3	33
Galvalume (#3 drawbar)	4-8	0	0	1	1	3	1

TABLE 7
Butler Water Immersion Test Results

(% Black Rust (BR) White Rust (WR))

Substrate/ Coating method	Total Coat. Wt. (mg/ft ²)	168 Hrs		336 Hrs		672 Hrs	
		BR	WR	BR	WR	BR	WR
HDG (#9 drawbar)	8-12	1	1	10	3	33	33
Galvalume (#3 drawbar)	4-8	1	1	3	3	33	3

TABLE 8
Neutral Salt Spray Test Results
(% Black Rust (BR) White Rust (WR))

5	Substrate/ Coating method	Total Coat. Wt. (mg/ft ²)	168 Hrs		336 Hrs		672 Hrs	
			BR	WR	BR	WR	BR	WR
	HDG (#9 drawbar)	8-12	0	0	1	10	3	33
10	Galvalume (#3 drawbar)	4-8	0	0	1	1	3	1

Note: BR, WR and RR corresponds to black rust, white rust and red rust.

15 The Stack testing, (ii) Butler Water Immersion testing were carried out as follows:

StackTest:

The panels were cut to 4" x 4" size.

20 Any duplicate test panels were stacked face-to-face with an amount of deionized water (as indicated in drops or as a spray) being applied between the two test panels to wet the surfaces.

The stack of test panels were clamped together in a test jig and tightened to about 50 in. •lb. torque.

The stack of panels were placed in a humidity test cabinet at 100°F and 100% humidity.

The test panels were evaluated at the time intervals shown in table 6 for black rust (BR) and white rust (WR).

Butler Water Immersion Test:

5 Samples were cut into 3-1/2" x 7-1/2" panels such that the samples support themselves on the sides of the glass tray approximately 1/2" from the bottom of the tray.

Metal surfaces that had been oiled were rinsed on both sides of the sample with naphtha and allowed to dry.

The samples were placed in the glass tray.

10 Enough distilled water was added to the tray to cover the sample with 3/4" of water.

The uncovered trays were placed in a humidity cabinet at 100% humidity and 100°F.

The top surfaces of the test panels were evaluated at the time intervals shown in table 7 for black rust and white rust.

Example 4

HDG steel test panels were cleaned with a 4 wt. % solution of Ridoline® 321 at a temperature of about 140°F for about 30 seconds. The panels were then hot water rinsed at a temperature of about 120°F for about 10 seconds.

5 The panels were then squeegeed dry. Compositions 1 and 4 were applied to the panels using various drawbars. The panels were then cleaned with a 4.5 wt. % solution of Parco® cleaner 1200 for about 30 seconds at about 150°F. The test panels were observed to be fully cleaned in accordance with the following procedure.

10 The cleaned test panels were rinsed with D.I. water and dried. A drop of about a 3 wt. % copper sulfate pentahydrate solution was dropped on the panels. A 100% reaction, evidenced by the area of the panel that contacts the drop turning black, within a second of contact, was observed on all the panels, indicating that the panels were fully cleaned.

15

Example 5

HDG steel test panels prepared in the same manner as set forth in Example 4 were then subjected to the following procedure and subjected to T-bend testing. The results are shown below in Table 9.

The procedure that was followed was:

20 A = pretreat 3 panels with Bonderite® 1402W, prime coat with UY9R 24235, and top coat with CLS 9872 from Akzo.

B= pretreat 3 panels with Bonderite® 1303 and Parcolene® 62, prime coat with UY9R 24235, and top coat with CL 9872 from Akzo.

C= treat 3 panels with Parcolene® AT, Bonderite® 1421, and Parcolene® 62, prime coat with UY9R 24235, and top coat with CLS 9872.

5 The T-bend test was carried out in accordance with ASTM D4145.

TABLE 9

T-bend results

10	Panels Treated With Bonderite® 1402W		Panels Treated With Bonderite® 1303		Panels Treated With Bonderite® 1421	
	Composition/ Panel ID	T-Bend	Composition/ Panel ID	T-Bend	Composition/ Panel ID	T-Bend
	Bare/ A1	1T	Bare / B1	0T	Bare/ C1	1T
	Bare/ A2	1T	Bare / B2	0T	Bare/ C2	1T
	Bare/ A3	1T	Bare / B3	0T	Bare/ C3	1T
15	1/ A1	2T	1/ B1	0T	1/ C1	1T
	1/ A2	2T	1/ B2	0T	1/ C2	1T
	1/ A3	2T	1/ B3	0T	1/ C3	1T
	3/ A1	2T	3/ B1	0T	3/ C1	1T
	3/ A2	3T	3/B2	0T	3/ C2	1T
20	3/ A3	2T	3/B3	0T	3/ C3	1T

0T is the best, 0T-2T are acceptable.

From the above results, it confirms that panels treated with the chrome free passivate of the present invention are treatable and paintable.

Example 6

5 HDG steel test panels were coated with composition 1. Samples C and D were cleaned with a 4.5 wt. % solution of Parco® cleaner 1200 for about 25 seconds at about 160°F. Samples C and D were subjected to the same test as set forth in Example 4 and were observed to be fully cleaned. The sample designations are shown below.

- A: Composition 1 treatment on HDG at high coating weights (8-16 mg/ft²).
- 10 B: Composition 1 treatment on HDG at low coating weights (4-8 mg/ft²).
- C: Sample A cleaned with Parco® Cleaner 1200.
- D: Sample B cleaned with Parco® Cleaner 1200.

15 The test panels were submitted to Evans Analytical Group™ for surface analysis using X-Ray Photoelectron Spectroscopy. The surfaces were analyzed as three depths- (i) as received, (ii) about 75 Å (angstroms) below the as received surface, and (iii) about 150 Å (angstroms) below the as received surface. Notably, the spectroscopy analysis confirmed that samples C and D were fully cleaned.

The results are shown below in Table 10.

Atomic concentrations of elements expressed in atomic percents

TABLE 10

		C	N	O	F	Na	Mg	Al	Si	P	Cl	Ca	Ti	Zn
Sample A	as-rec'd	31.6	0.9	42.6	4.9	-	0.2	0.3	-	7.4	-	-	3.1	9.0
Sample A	~ 75 Å	1.9	-	52.3	8.2	-	0.2	1.0	-	10.0	-	-	8.5	17.9
Sample A	~ 150 Å	0.9	-	51.8	9.3	-	0.3	0.9	-	9.6	-	-	9.4	17.9
Sample B	as-rec'd	25.9	tr	37.7	13.9	1.1	0.5	1.8	-	5.4	-	0.2	3.7	10.0
Sample B	~ 75 Å	1.4	-	52.9	8.3	-	0.2	1.9	-	7.8	-	-	11.0	16.6
Sample B	~ 150 Å	1.1	-	53.6	7.7	-	0.3	2.1	-	8.0	-	-	11.3	16.0
Sample C	as-rec'd	20.4	tr	52.7	-	-	0.5	-	0.5	0.4	0.3	0.4	-	24.8
Sample C	~ 75 Å	2.5	-	39.6	-	-	-	0.6	-	-	-	0.2	-	57.1
Sample C	~ 150 Å	1.7	-	22.3	-	-	-	0.1	-	-	-	-	-	75.9
Sample D	as-rec'd	29.7	tr	49.4	-	-	0.6	-	-	-	-	0.3	-	20.1
Sample D	~ 75 Å	2.6	-	40.3	-	-	0.7	1.0	-	-	-	0.6	-	54.8
Sample D	~ 150 Å	3.7	-	23.2	-	-	-	0.7	-	-	-	0.2	-	72.3

"-" = not detected "tr" = trace amount detected

While embodiments of the invention have been illustrated and described, it is not intended that these embodiments illustrate and describe all possible forms of the invention. Rather, the words used in the specification are words of description rather than limitation, and it is understood that various changes may be made without departing from the spirit and scope of the invention.